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## DIELECTRIC PROPERTIES OF SOME BENT CORE LIQUID CRYSTALS

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### Abstract

Dielectric measurements were carried out on a series of bent-core liquid crystals based on resorcinol and 2, 7-dihydroxynaphthalene cores and presenting B mesophase in between 30-160°C. The dielectric constants in the liquid crystalline phase were measured as a function of frequency and temperature. The dielectric relaxation of bent-core compounds has been analyzed by dielectric constants/frequency curves. The variation of the dielectric strength with temperature has been determined as well. The frequency dependence of dielectric loss has also been analyzed by means of frequency exponent.

*Key words:* bent-core liquid crystals, dielectric spectroscopy, molecular reorientation

*Received:* May, 2017; *Revised final:* January, 2018; *Accepted:* March, 2018; *Published in final edited form:* April 2018

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### 1. Introduction

The liquid crystalline phase is a thermodynamic stable state of matter that exhibits the anisotropic properties of crystals, due to the orientational ordering and flow properties of liquids, derived from the mobility of the molecules. The ordered structures of anisotropic molecules cause as well anisotropy in their physical properties, as the dielectric constant and optical birefringence. As a result, in the presence of an electric field, the anisotropy of the dielectric permittivity leads to the reorientation of liquid crystal molecules. In liquid crystals with positive dielectric anisotropy, the director reorients parallel to an applied electric field, while for negative dielectric anisotropy, the director is perpendicular to the electric field. Generally, liquid crystals which denote positive dielectric anisotropy at low frequencies are used for the most active matrix

displays for image quality of LCDs (Kelly and O’Neil, 2000).

The response of a liquid crystalline material is in concordance to the magnitude of the dielectric permittivity, which in turn depends on the temperature and the frequency of the applied field in the mesophase (Kundu et al., 2007; Marik et al., 2015; Sreenilayam et al., 2015; Yildiz et al., 2016a, 2016b; Yilmaz Canli et al., 2015). The relationship between dielectric constant and molecular properties of liquid crystals provides useful information in determining the electro-optical response of devices based on liquid crystals, which should combine birefringence, high dielectric anisotropy and low viscosity (Reddy and Tschierske, 2006; Takezoe and Takanishi, 2006; Tschierske, 2013). In this regard, dielectric spectroscopy is used to obtain reliable information towards the molecular structure, dynamics of polar structures, phase transitions and switching speed performances of liquid crystals. Parameters which

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decide whether a material is suitable for technological applications are the real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) part of dielectric function, dielectric loss ( $\tan\delta$ ) and conductivity ( $\sigma$ ). For instance, relatively higher dielectric constants are used in microelectronics devices such as memory devices (Kelly and O'Neil, 2000).

After the discovery of electro-optical switching in the mesophases of bent core achiral molecules as a result of spontaneous chirality (Niori et al., 1996), numerous studies have been focused on designing of banana type molecules (Link et al., 1997; Sadashiva, 2014; Weissflog et al., 2001; Weissflog et al., 2006).

There are some factors that influence the mesomorphic properties and therefore the dielectric properties of liquid crystalline materials, as the geometry of molecules and the nature of rigid core, lateral polar substituents or terminal flexible chains (Demus, 1998). Although the structure-property correlations are well established for calamitic liquid crystals, for bent core liquid crystals steric effects exercise a significant influence on some of the physical properties such as viscosity. Consequently, factors as the size of the molecules, the position and the magnitude of the angle of bent central unit ( $135$  to  $140^\circ$ ) should be taken into account (Pelzl et al., 1999). However, because the mesophases formed by bent core molecules often occurs above  $150^\circ\text{C}$ , it is difficult to determine their physical properties. Among mesophases showed by banana-shaped molecules, the B2 phase has been associated with specific dielectric properties (Krishna Prasad et al., 2003; Pelzl et al., 1999). In the present study, the electric fields that induced effects on mesophases properties of some bent core liquid crystals based on resorcinol (DCB) and 2,7-dihydroxynaphthalene (RAC and CAN) (Fig. 1) were studied. In this regard, the relaxation behavior of static parameters as permittivity ( $\epsilon$ ) and dielectric loss tangent ( $\tan \delta$ ) were measured as a function of frequency and temperatures into mesophase.

## 2. Material and methods

Synthesis and liquid crystalline properties of compounds DCB, RAC and CAN were previously reported (Simion et al., 2015, 2016). The dielectric measurements were conducted on a Novocontrol Alpha-A Frequency Analyzer, connected to planar cell filled with liquid crystalline material that was heat from  $30^\circ\text{C}$  to isotropization temperatures.

The experimental data were registered only on first heating in the frequency range  $1$  Hz and  $10^6$  Hz. The samples were grounded using an agate mortar and pressed between two electrodes using a 15T manual hydraulic press. The thickness was determined using a micrometer screw (Mitutoyo Absolute, model ID-C112X,  $12.7 - 0.001$  mm range).

## 3. Results and discussion

### 3.1. The liquid crystalline properties of the investigated bent core compounds

The dielectric behavior of the compounds has been studied over a range of frequency and temperature mesophases. All the investigated bent-core compounds presented a good thermal stability and a convenient temperature range of liquid crystalline phase. According to DSC analysis correlated with POM textures, compound CAN exhibited the widest mesophase range (about  $30^\circ\text{C}$ ) towards RAC and DCB, proving that the presence of disubstituted 2,7-naphthalene central unit better stabilizes mesophases than disubstituted 1,3-benzene core.

However, the presence of disubstituted 1,3-benzene core in compound DCB lowers the temperature when liquid crystalline phase appears on heating, with a temperature difference of about  $40^\circ\text{C}$ , if compared with the others two compounds (Fig. 2).

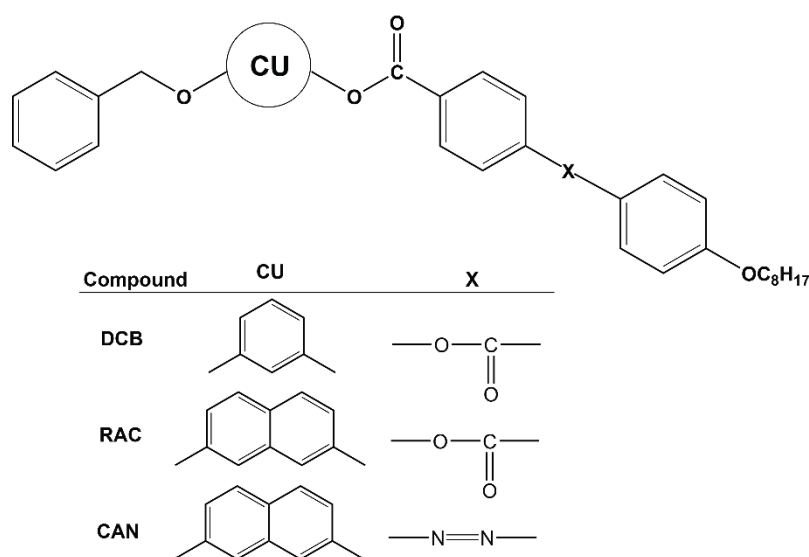


Fig. 1. General structure of studied bent core liquid crystals (CU: central unit)

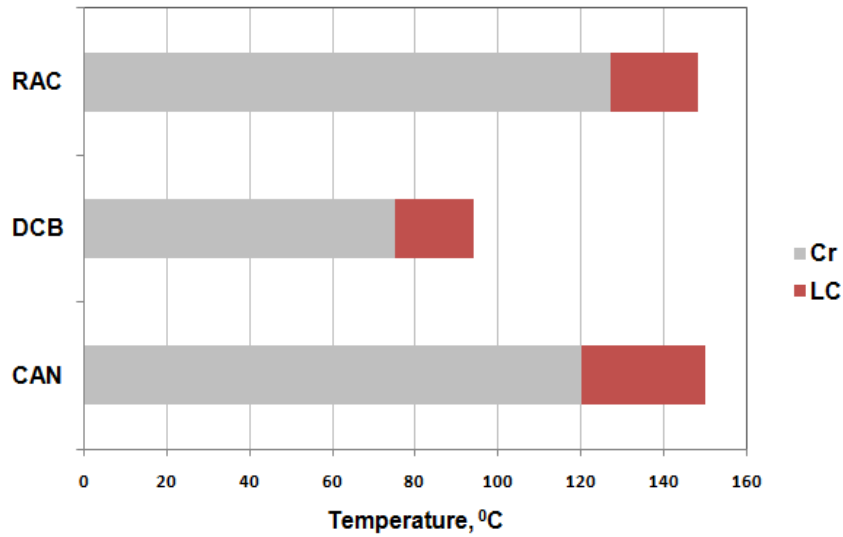


Fig. 2. The liquid crystalline domains of bent core compounds obtained by differential scanning calorimetry (10°C/min) on heating Cr = crystal, LC = liquid crystal

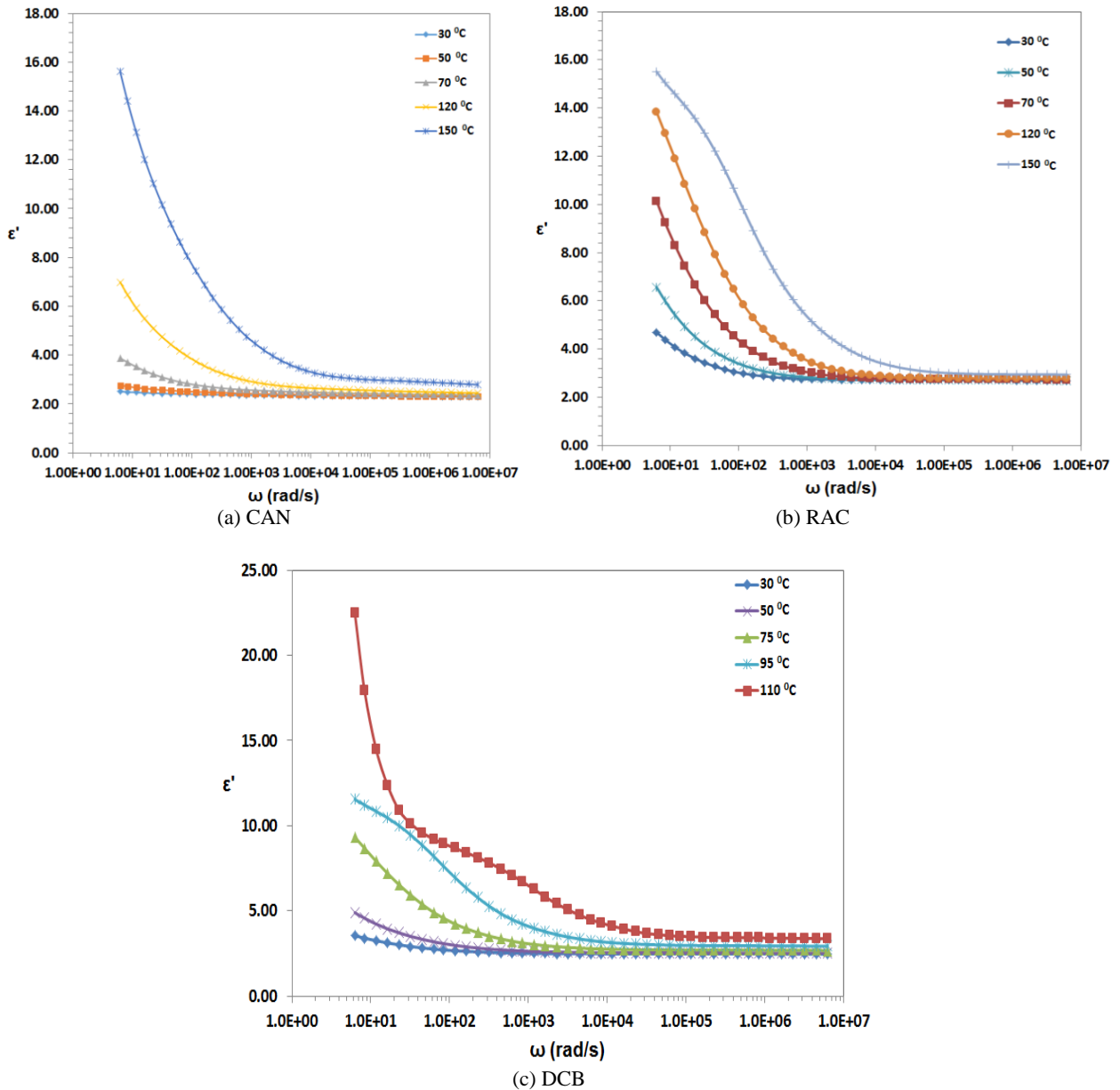


Fig. 3. The angular frequency dependence of the real parts of the dielectric constant of the investigated bent-core liquid crystals as a function of temperature

### 3.2. Analysis of temperature effect on dielectric parameters of the investigated bent-core liquid crystals

The dielectric parameters of the investigated bent-core liquid crystals have been measured within the frequency interval of 1 - 10<sup>6</sup> Hz at various temperatures varying from 30°C to 160°C. In this respect, dielectric parameters of CAN have been compared with DCB and RAC. The frequency dependences of the real part of dielectric constant ( $\epsilon'$ ) are presented in Fig. 3 (where  $\omega = 2\pi f$  and  $f$  is the linear frequency). The obtained data suggest that  $\epsilon'$  shows dispersive behavior and decreases gradually with the increases of frequency and then attains to close values at high frequencies, a characteristic behavior of dielectric materials (Sinha et al., 2001). On the other hand, the real part of dielectric constant has its maximum value at low frequencies. The explanation is that at high frequencies (i.e.  $> 10^4$ ), the molecular agitation is high so there is no dipolar polarization. As a result, noticeable loss of stored energy appears; hence the  $\epsilon'$  approaches the same low values. However, at low frequencies, the existence of a net molecular polarization leads to increases of the real parts of the dielectric constant that increases with temperatures, due to the molecular reorientation.

The variation of the real parts of the dielectric constant of the investigated bent-core compounds with temperature in different frequency regions (1 kHz, 5 kHz, 10 kHz, 100 kHz) is presented in Fig. 4, in the whole investigated temperature range in the heating process. The temperature dependence of dielectric permittivity shows potentially phase transitions.

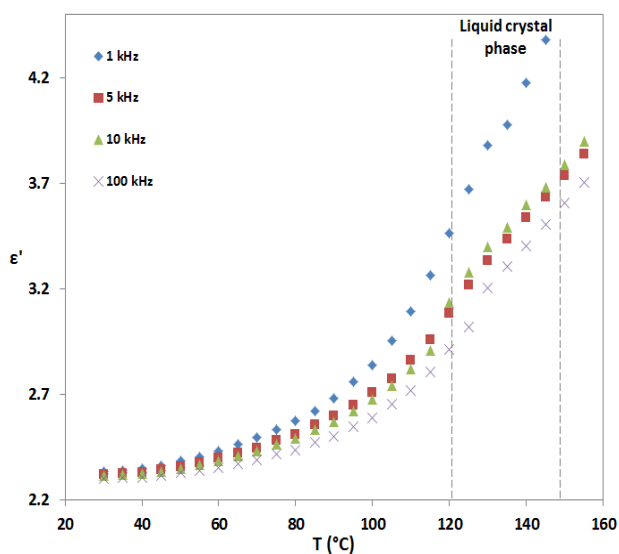
Although the three compounds have different liquid crystalline phase temperature domains, the dielectric constants deviate from the linear shape and start increasing gradually with temperature after 55°C, suggesting some similar phase transition of crystal-crystal type for all bent-core compounds, more

pronounced for RAC. In liquid crystalline phases, the dielectric constants reach the maximum values at 1 kHz, when the polarization is probably high as well.

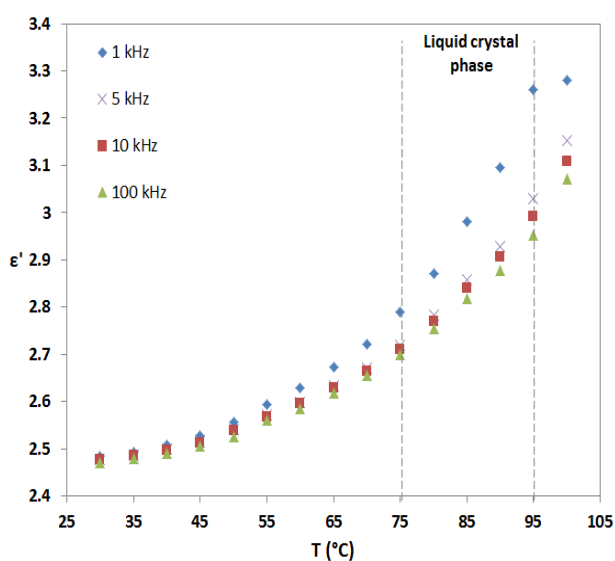
The angular frequency dependence of the imaginary component of the dielectric constant (dielectric loss) has been given as well (Fig. 5). As shown, the magnitude of the imaginary parts of dielectric constant in the low frequency region is higher than that of high frequency region. In the high frequency regions, the imaginary components of dielectric constant have small hollows (more pronounced for RAC and DCB), between 10<sup>4</sup> and 10<sup>6</sup> Hz, corresponding to dielectric relaxations. Since the magnitude of  $\epsilon''$  is proportional to energy dissipation, it was assumed that bent-core liquid crystals are more stable in the high frequency region.

Moreover, the dissipation energy has been analyzed in the conduction process. The electrical conductivity  $\sigma$  is known to be related to dielectric loss  $\epsilon''$ , depending on frequency and temperature as well. As shown in Fig. 6, conductivity ( $\sigma$ ) has a tendency of increase both with temperature and frequency. This phenomenon can be useful in liquid crystal device applications. In addition to this, as the frequency increases, the conductivity increases about linearly to 10<sup>5</sup> Hz, when the growth deviates appreciably and attains to similar value.

It is noticeable that conductivity curves show similar behavior for RAC and DCB while the deviations for CAN are less evidenced. The highest conductivity values of corresponding mesophases, at the frequency of 10<sup>5</sup> Hz have similar order sizes as follow:  $\sigma_{RAC} = 2.39 \times 10^{-9}$  S/cm,  $\sigma_{DCB} = 2.12 \times 10^{-9}$  S/cm and  $\sigma_{CAN} = 1.108 \times 10^{-9}$  S/cm. One should point out that conductivities in crystalline phases (at 30 °C) are by two orders of magnitude smaller than that ones from mesophases:  $\sigma_{RAC} = 8.95 \times 10^{-11}$  S/cm,  $\sigma_{DCB} = 8.02 \times 10^{-11}$  S/cm and  $\sigma_{CAN} = 7.08 \times 10^{-11}$  S/cm. These data are important for applications.



(a) CAN



(b) DCB

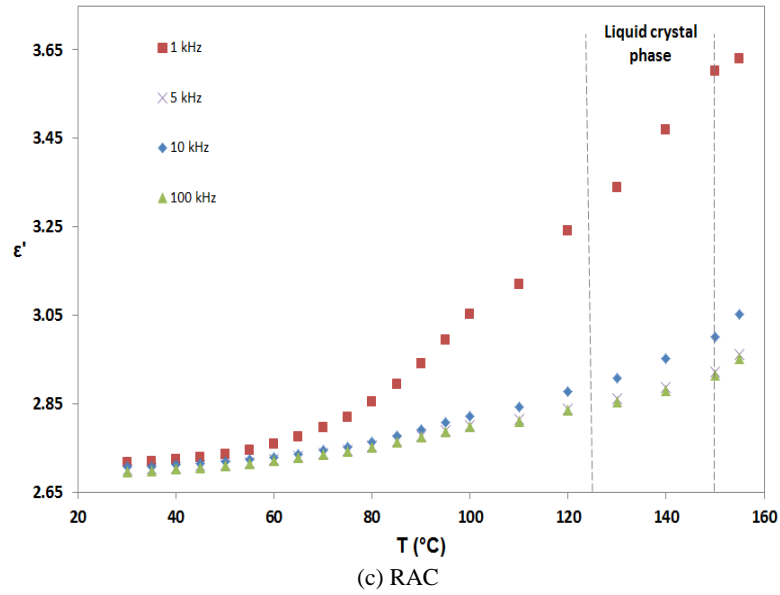


Fig. 4. Temperature dependence of the real parts of the dielectric constant of the investigated bent-core liquid crystals at different frequencies

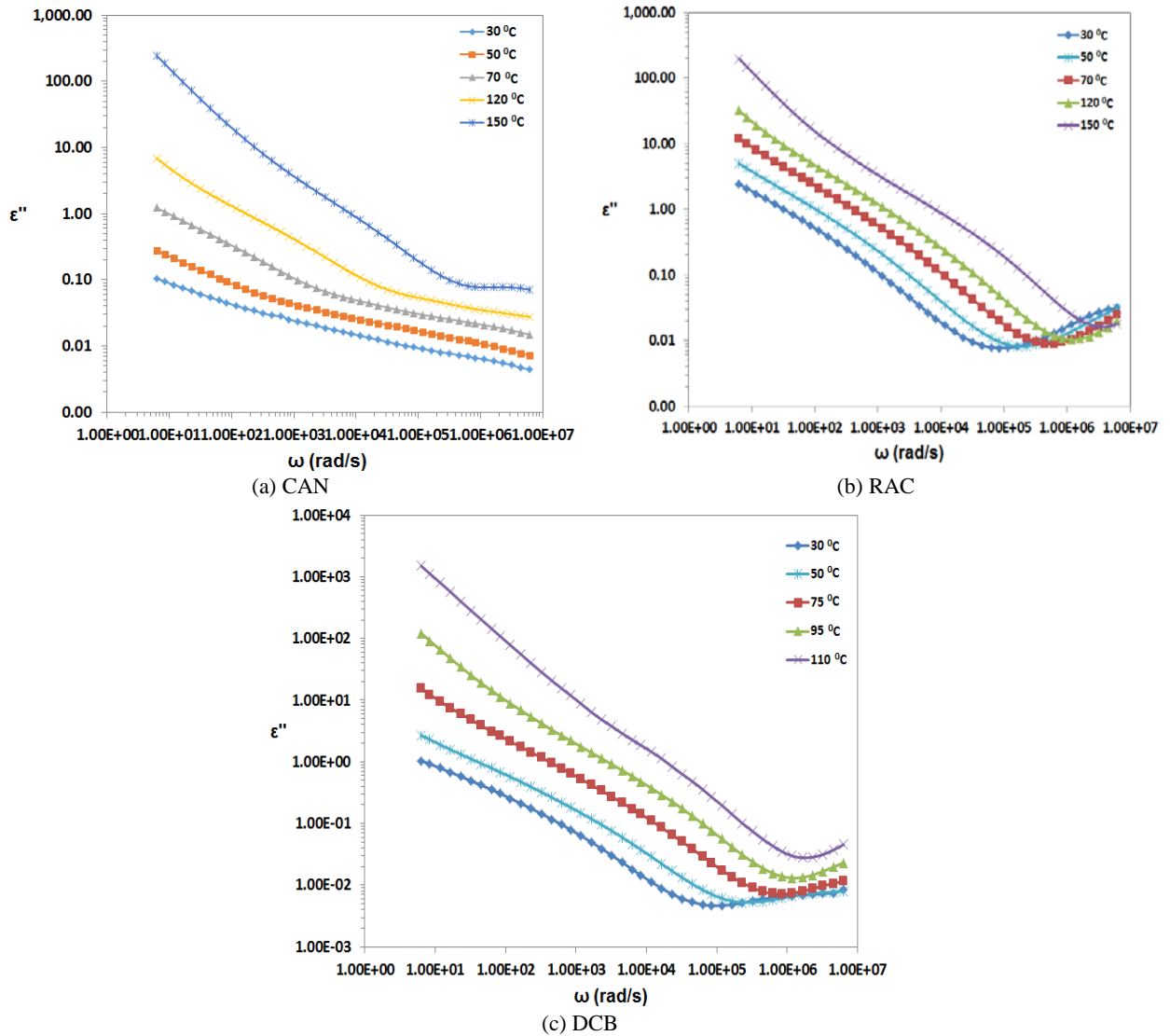


Fig. 5. The angular frequency dependence of the imaginary parts of the dielectric constant of the investigated bent-core liquid crystals at different temperatures

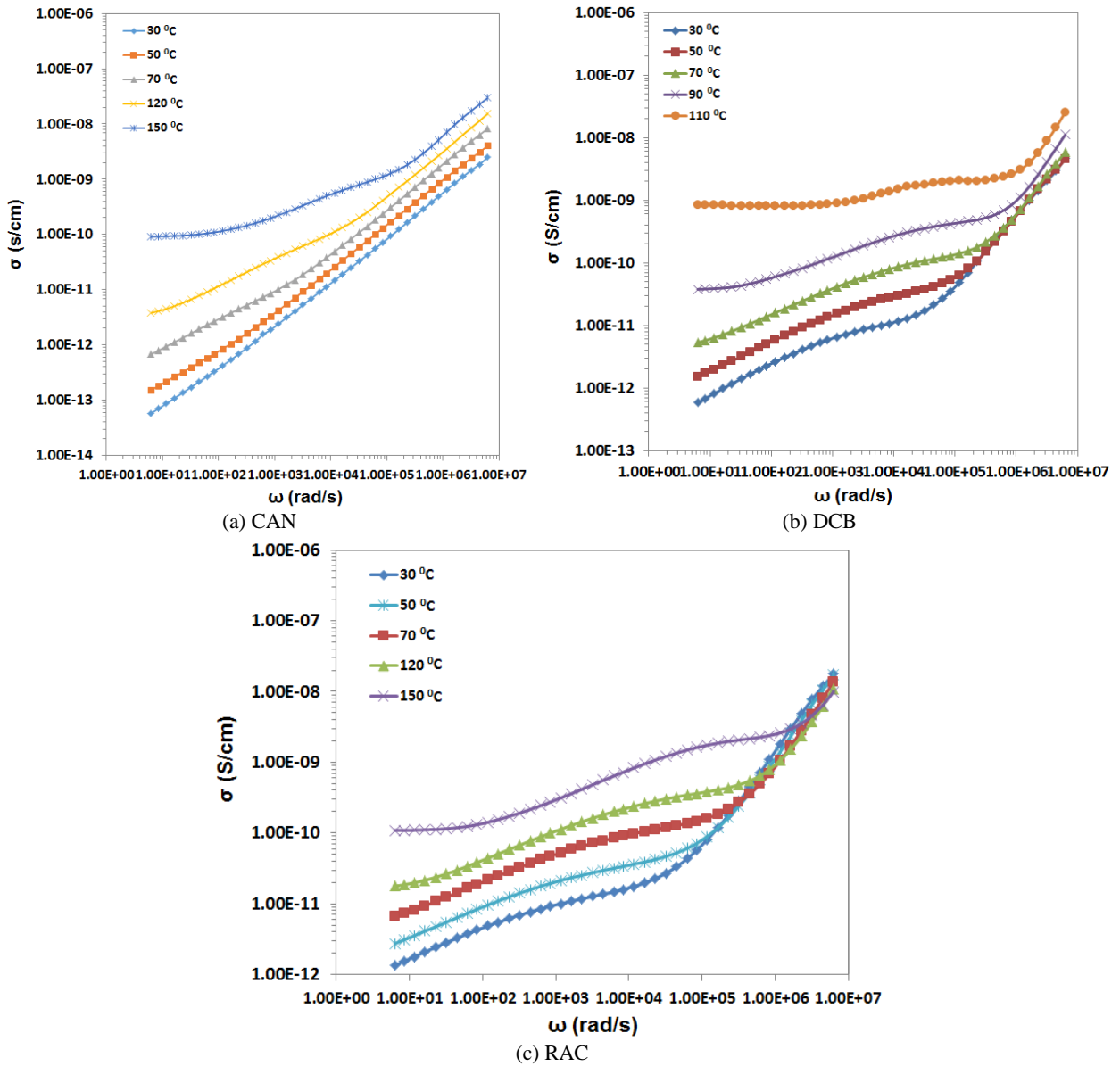
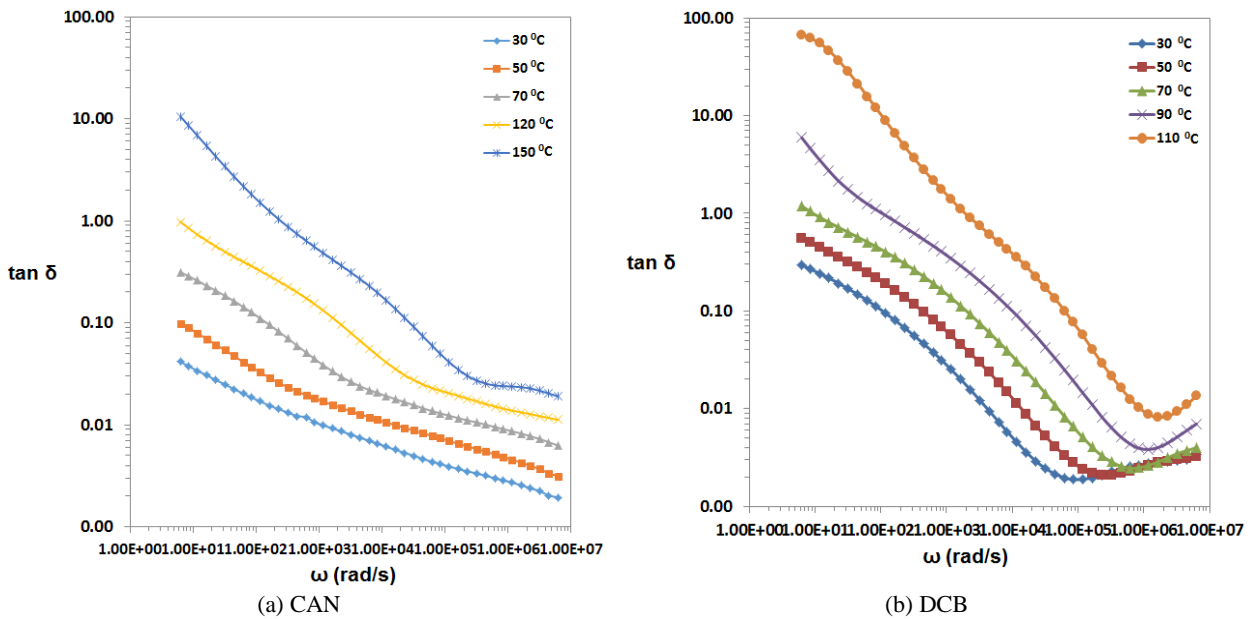


Fig. 6. Angular frequency dependence of the real part of conductivity for bent-core liquid crystals at different temperatures





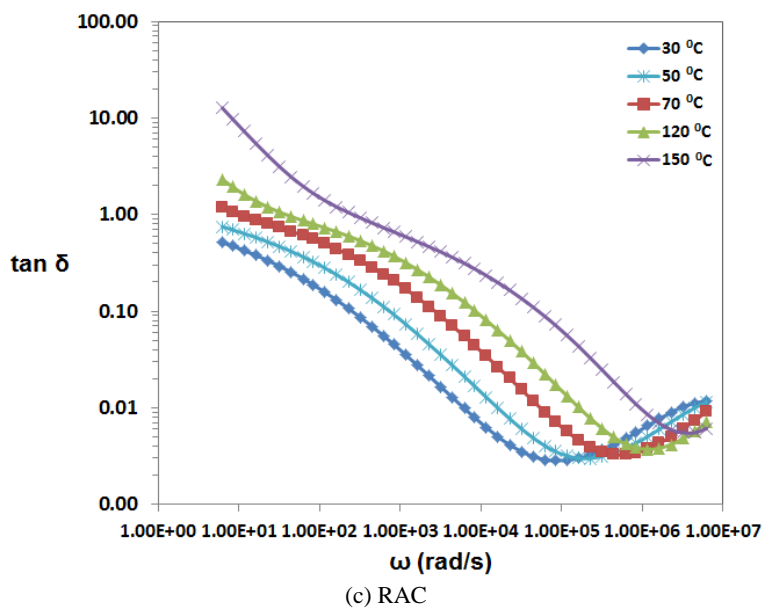


Fig. 7. The angular frequency dependence of the dissipation factor at different temperatures

### 3.3. Analysis of frequency effect on dissipation factor

The frequency and temperature dependence of dissipation factor (dielectric loss tangent) was also analyzed (Fig. 7). For all the compounds, the relaxation processes are found between  $10^4$  and  $10^6$  Hz. As shown in Fig. 7, the dissipation factors vary in about a similar way with the imaginary components of dielectric constant, but the loss peaks corresponding to dielectric relaxations are more pronounced. Thus, CAN show some poor relaxation peaks between  $120^\circ\text{C}$  and  $150^\circ\text{C}$ , the mesophase domain, where also has the highest values of  $\tan \delta$ . In contrast to CAN, the relaxation processes corresponding to DCB and RAC are more emphasized, and what is obvious, not only on mesophase domains. This different behavior between the compounds reflects the various physical interactions which take place, more intensive in DCB and RAC. It can be assumed that the presence of an esteric linkage between the two aromatic rings enhances the delocalization of the electronic cloud with the increase of the molecular dipole moment. As result, these molecules can be easily reoriented.

## 4. Conclusions

In the present study, the dielectric properties of some bent-core liquid crystals were studied as a function of temperature and frequency. The angular frequency dependence of the real and imaginary components of dielectric constant and the dielectric strength has been analyzed for the low and high frequency regions.

The investigated bent-core compounds are easier reoriented in the high frequency domain, where are more stable. The conductivity in mesophases is much higher than in crystalline state, proving the potential uses of bent-core liquid crystals in applications. Compounds with esteric linkage between

aromatic rings display more emphasized relaxation processes, for the whole temperature domains, probably due to electronic delocalization.

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